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Dynamics of critical concentration fluctuations in gels

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The dynamics of concentration fluctuations in a gel near phase separation is described by a mode-coupling theory. The scaling relations, $E \propto 1/\xi^2$ and $f \propto 1/\xi$, where ξ is the correlation length of the concentration fluctuations in the network, are obtained for the elastic constant of the network, E, and the frictional coefficient between the network and the fluid medium, f. The theory fully explains the experimental results of Tanaka, Ishiwata, and Ishimoto on a polyacrylamide gel.

INTRODUCTION

A gel is an infinite cross-linked polymer network immersed in a fluid medium. The polymer network concentration undergoes thermal fluctuations in space and time. Recently, Tanaka, Ishiwata, and Ishimoto (TII) observed a critical divergence and slowing down of concentration fluctuations in polyacrylamide gel using laser light scattering spectroscopy[1]: Both the intensity and the correlation time of the scattered light increase as temperature decreases and appear to diverge at a certain temperature. It was explained as critical behavior associated with a phase separation of the binary mixture of the network and the fluid medium, namely, a shrinkage of the network in a fluid medium.

In this paper we present a detailed theory of the dynamics of concentration fluctuations in gels near phase separation. We calculate the time correlation function of the concentration fluctuations in the network by following the procedure of the mode coupling theory developed by Kawasaki.[2] (See also the equivalent theory by Ferrell.[3]) Their results have been successfully applied to explaining the dynamical behavior of critical fluid mixtures.[4] An essential difference between gels and fluid mixtures lies in the presence of shear elasticity in gels, which is absent in fluid mixtures. It will be shown, however, that this difference has little influence on concentration fluctuations of wavelength comparable to that of visible light. The results of the present theory are in excellent agreement with the observation of TII. The scaling relations for the viscoelastic parameters of gels will be obtained by comparing this theory with the macroscopic theory of the dynamics of gels by Tanaka, Hocker, and Benedek (THB).[5]

THEORY

The polymer network can be considered as a homogeneous elastic body since the average distance between adjacent cross-link points (several hundred angstroms) is an order of magnitude less than the wavelength of visible laser light. The network concentration $\rho(\vec{r}, t)$ must satisfy the equation of mass conservation:

$$\frac{\partial \rho(\vec{r},t)}{\partial t} = \vec{\nabla} \cdot [\rho(\vec{r},t)\vec{v}(\vec{r},t)] \ , \tag{1}$$

where $\vec{v}(\vec{r},t)$ is the local velocity of the polymer network. Kawasaki[2] has derived from Eq. (1) a general formula for the correlation function of the concentration fluctuations,

$$\langle \Delta\rho^2[\vec{q},\omega]\rangle = \langle \Delta\rho^2[\vec{q}]\rangle / (-i\omega - \Sigma[\vec{q},\omega]) \ , \tag{2}$$

where $\vec{q}$ is the wave vector, ω is the frequency, $[\vec{q},\omega]$ denotes the Fourier transform in space and time, and $[\vec{q}]$ denotes the Fourier transform in space only. Σ is called the self-energy and is given as

$$\Sigma[\vec{q},\omega] = -q^2 \frac{k_B T}{\rho_g} \int \frac{d\vec{k}}{(2\pi)^3} \left[1 - \left(\frac{k_z}{k}\right)^2\right] \frac{\langle \Delta\rho^2[\vec{q}-\vec{k}]\rangle}{\langle \Delta\rho^2[\vec{q}]\rangle} \times \frac{\langle v^2[\vec{k},\omega]\rangle}{\langle v^2[\vec{k}]\rangle} \ , \tag{3}$$

where k_B is the Boltzmann constant, T is the absolute temperature, ρ_g is the density of the whole gel, and v is the amplitude of shear displacement velocity. The direction of the wave vector $\vec{q}$ is chosen as the z axis. To obtain the correlation function $\langle \Delta\rho^2[\vec{q},\omega]\rangle$ we must know both the static correlation function $\langle \Delta\rho^2[\vec{q}]\rangle$, and the correlation function of the amplitude of shear displacement velocities $\langle v^2[\vec{k},\omega]\rangle$. We assume that the former can be given by the formula of Ornstein and Zernike,[6]

$$\langle \Delta\rho^2[\vec{q}]\rangle = A\left(\frac{\xi}{R}\right)^2 \frac{1}{1+q^2\xi^2} \ , \tag{4}$$

where ξ is the long-range correlation length of the concentration fluctuations, the constant R is the Debye persistence length, and A is a constant.

The latter can be calculated as follows. The shear displacement velocity obeys the following equation of motion:

$$\rho_g \frac{\partial v}{\partial t} = \eta \frac{\partial^2 v}{\partial x_k^2} - \mu \frac{\partial^2 u}{\partial x_k^2} , \tag{5}$$

where u is the amplitude of the shear displacement, x_k denotes the coordinate in the direction of the wave vector $\vec{k}$ of the shear wave, η is the viscosity of the gel, and μ is the shear modulus of the gel. In the absence of the term $\mu \partial^2 u/\partial x_k^2$ representing the elastic restoring force, Eq. (5) reduces to the equation for shear waves in a fluid. The solution of Eq. (5), with the initial condition $\langle u[\vec{k}, t=0] v[\vec{k}, t=0]\rangle = 0$, is

$$\frac{\langle v^2[\vec{k}, \omega]\rangle}{\langle v^2[\vec{k}]\rangle} = \frac{1}{\Gamma_+ - \Gamma_-}\left(\frac{\Gamma_+}{-i\omega - \Gamma_+} - \frac{\Gamma_-}{-i\omega - \Gamma_+}\right), \tag{6}$$

where

$$\Gamma_\pm = \frac{\eta k^2}{2\rho_g}\left[1 \pm \left(1 - \frac{4\mu\rho_g}{\eta^2 k^2}\right)^{1/2}\right]. \tag{7}$$

From macroscopic measurements of the period and the decay rate of shear oscillation ($k \sim 1\ \text{cm}^{-1}$) of a 2.5% polyacrylamide gel, we determined that $\eta \sim 3$ cP and $\mu \sim 200\ \text{dyn/cm}^2$ at room temperature, which gives $4\mu\rho_g/\eta^2 \sim 10^6\ \text{cm}^{-2}$. With this value the integrand in Eq. (3) has a smooth distribution in k space and the average value of k^2 is approximately $k_0^2 \equiv q^2 + 1/\xi^2 \gtrsim 10^{10}\ \text{cm}^{-2}$. Thus, for k which contributes to the integration, where $4\mu\rho_g/\eta^2 \ll k^2$, Eq. (6) reduces to

$$\frac{\langle v^2[\vec{k}, \omega]\rangle}{\langle v^2[\vec{k}]\rangle} \simeq \frac{1}{-i\omega - \eta k^2/\rho_g} , \tag{8}$$

which can be further approximated as

$$\frac{\langle v^2[\vec{k}, \omega]\rangle}{\langle v^2[\vec{k}]\rangle} \simeq -\frac{\rho_g}{\eta k^2} , \tag{9}$$

since $\eta k_0^2/\rho_g \sim 3 \times 10^8$ Hz is much larger than the frequency range of concentration fluctuations observed in the light-scattering experiment by TII ($\omega \sim 3 \times 10^5$ Hz). It is important to note that the shear modulus μ does not appear in Eq. (8) since for $k \simeq k_0$ the term representing the shear restoring force in Eq. (5) is negligible.

Integrating Eq. (3) using Eqs. (4) and (9), we now obtain the correlation function (see Ref. 2)

$$\langle \Delta\rho^2[\vec{q}, \omega]\rangle = A\left(\frac{\xi}{R}\right)^2 \frac{1}{1 + q^2\xi^2} \frac{1}{-i\omega - \Gamma} , \tag{10}$$

where

$$\Gamma = \frac{k_B T}{6\pi\eta\xi^3} K(q\xi) , \tag{11}$$

and $K(x) = \frac{3}{4}[1 + x^2 + (x^3 - 1/x)\arctan x]$. In the hydrodynamic regime ($q\xi \ll 1$), this can be written as

$$\langle \Delta\rho^2[\vec{q}, \omega]\rangle = A\left(\frac{\xi}{R}\right)^2 \frac{1}{-i\omega - (k_B T/6\pi\eta\xi)q^2} . \tag{12}$$

COMPARISON WITH EXPERIMENTS

Let us now compare this theoretical prediction, $\Gamma = (k_B T/6\pi\eta\xi)q^2$, with the experimental observa-

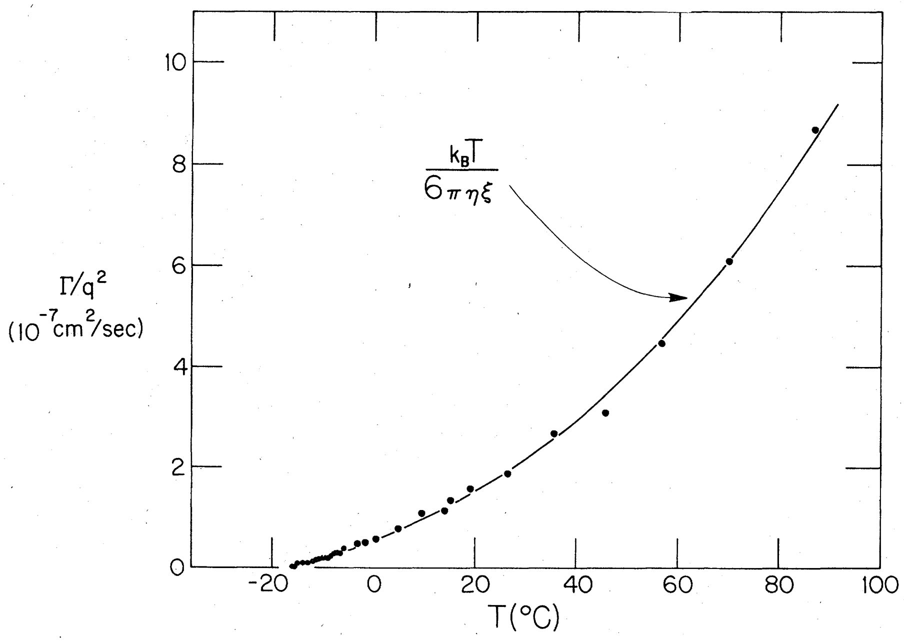

FIG. 1. Decay rate Γ/q^2 of concentration fluctuations in a 2.5% polyacrylamide gel measured by Tanaka, Ishiwata, and Ishimoto using laser light scattering spectroscopy (Ref. 1). The solid line is the prediction of the present theory: $\Gamma/q^2 = k_B T/(6\pi\eta\xi)$.

tions of TII. From the intensity of light scattered from the gel, TII found that $\langle \Delta\rho^2[\vec{q}] \rangle \propto T/(T-T_s)$ for $q\xi \ll 1$, where T_s is the spinodal temperature, at which the amplitude of concentration fluctuations diverges. From Eq. (4) we see that $\langle \Delta\rho^2[\vec{q}] \rangle \propto \xi^2$ for $q\xi \ll 1$. Thus

$$\xi = \xi_0[T/(T-T_s)]^{1/2} , \tag{13}$$

where ξ_0 is a constant. This expression corresponds to the result of the mean field theory.[1] Since the concentration of the polymer network (2.5%) is very low, η may be taken to be proportional to the viscosity of water, $\eta_w(T)$,

$$\eta = [\eta(20\,^\circ\mathrm{C})/\eta_w(20\,^\circ\mathrm{C})]\,\eta_w , \tag{14}$$

where $\eta(20\,^\circ\mathrm{C})$ is approximately 3 cP, as stated above. In Fig. 1 the decay rate Γ/q^2 experimentally measured by TII, and $\Gamma/q^2 = k_B T/(6\pi\eta\xi)$ calculated from Eqs. (13) and (14) are plotted against temperature (ξ_0 was chosen to be 11 Å).[7] There is excellent agreement throughout the temperature range of the measurements.

DISCUSSION

In order to examine the viscoelastic properties of a gel near phase separation, we compare Eq. (12) with the result of the macroscopic theory on concentration fluctuations of a gel by THB[5,8]:

$$\langle \Delta\rho^2[\vec{q},\omega] \rangle = A\,\frac{Nk_BT}{E}\,\frac{1}{-i\omega-(E/f)q^2} , \tag{15}$$

where N is a constant proportional to the number of segments constituting the polymer network, and E and f are macroscopic parameters. E is the longitudinal osmotic elastic modulus of the network and f is the frictional coefficient of the network in the fluid medium: f times the velocity of the network relative to the fluid medium is the drag force exerted on the unit volume of the network. From the comparison, we see that

$$E = N_0(\xi_0/\xi)^2 k_B T \tag{16}$$

and

$$f = N_0(\xi_0/\xi)^2 6\pi\eta\xi , \tag{17}$$

where $N_0 = N(R/\xi_0)^2$. It is interesting that these expressions are the same as those for an ideal solution of $N_0(\xi_0/\xi)^2$ spheres with radius ξ. Equations (16) and (17) can be interpreted in the following way: the network of a gel consists of N_0 unit segments. At high temperature, where $\xi \simeq \xi_0$, these unit segments undergo diffusive movements independently. As temperature decreases and approaches the phase-separation temperature, the movements of the unit segments become correlated over a distance ξ. There are $N_0(\xi_0/\xi)^2$ such correlated regions which undergo independent diffusive movements. This $(\xi_0/\xi)^2$-dependence is due to the nonuniform concentration distribution in the correlated region used in the Ornstein-Zernike theory.[6] If the concentration were uniform in the correlated region, the number of regions should be proportional to $(\xi_0/\xi)^3$.

Tanaka, Ishiwata, and Ishimoto determined the elastic modulus E as a function of temperature from measurements of light intensity scattered by a 2.5% polyacrylamide gel.[1] By comparing their results with Eq. (16) it is found that N_0 is 1.3×10^{18} cm^{-3}. This indicates that approximately 60 mono-acrylamide molecules constitute one unit segment. The rms end-to-end distance of the unit segment is 15 Å$\simeq\sqrt{60}\times 2$ Å if it is assumed that the molecules (size ~2 Å) are connected through flexible bonds. This value roughly agrees with the value $\xi_0 = 11$ Å we have used in calculating the decay rate Γ.

In conclusion, it has been demonstrated that the dynamics of concentration fluctuations in the polymer network of a gel near phase separation can be well described by the mode-coupling theory. By comparing the present theory with the macroscopic theory of THB, the critical behavior of the viscoelastic properties of gels has been clarified.

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[7] ξ_0 may be considered to represent the size of segments constituting the network polymers. The value ξ_0

=11 Å is comparable to 5.8 Å found in the critical solution of polystyrene in cyclohexane by W. Kuwabara, J. Kojima, and M. Kaneko, Phys. Rev. A 12, 2606 (1975).

[8] The decay rate $(E/f)q^2$ shown in Eq. (15) can also be obtained by substituting into Eq. (1) the "terminal velocity", $\vec{v}=\vec{F}/f=(E\vec{\nabla}\rho/\rho)/f$, where $\vec{F}$ denotes the elastic restoring force.